

JAPANESE

[JP,07-292321,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT
OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE
CORRECTION OR AMENDMENT

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the constituent for coating which can form the coating membrane which was excellent also in flexibility, the thickness limit, and the low price with heat resistance, hardness, and adhesion.

[0002]

[Description of the Prior Art]In order to acquire an advanced heatproof, abrasion proof, and corrosion resistance, an organic system paint is insufficient and ceramics system coating is used. Conventionally, as a formation method of ceramics system coating, PVD(s) (sputtering technique etc.), CVD, a sol-gel method, a poly CHITANO carbosilane system paint, a poly(JISHIRU) silazane system paint, a polysilazane system paint, a poly metalaw silazane system paint, etc. are known.

[0003]On the other hand, in order to acquire flexibility and transparency, the various organic system paints which used acrylic resin and added various fillers if needed are known. The heat resistance paint which blended the inorganic filler etc. with the ceramics precursor resin which consists of silicon compounds, such as polycarbosilane resin, polysilazane resin, and poly rag siloxane resin, and a fluoro-resin is also proposed (JP,4-168175,A and 5-156176 gazette).

[0004]

[Problem(s) to be Solved by the Invention]Ceramics system coating of pliability, a thickness limit, and a price is insufficient although excelled in heat resistance, hardness, and adhesion. On the other hand, although the acrylic resin system paint is excellent in pliability, the thickness limit, and the price and hardness improves to some extent with addition or the hardening agent of an inorganic filler, there is a limit and heat resistance, adhesion, etc. are insufficient.

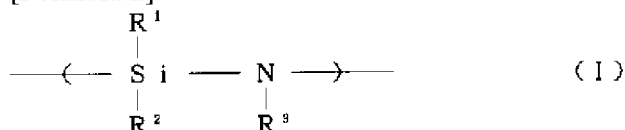
[0005]Since the silicon compound containing an organic group is used for said each of heat resistance paints which blended ceramics precursor resin and various resin, still, their effect over heat resistance, hardness, and adhesion is not enough. Since the

crack accompanying a pinhole or contraction occurs by desorption of the organic group at the time of baking especially, a film precise enough is not obtained but adhesion with a substrate also runs short. In said heat resistance paint, it is indispensable to add an inorganic filler or glass fiber, and in order not to contribute at all to the adhesion of what can raise hardness by these, the more it adds, the more adhesion and flexibility fall.

[0006]This invention solves these problems and an object of this invention is to provide the coating composition which gives coating membrane with the inorganic matter / organic hybrid structure where it excelled in flexibility, transparency, the thickness limit, and the price with heat resistance, hardness, and adhesion.

[0007]
[Means for Solving the Problem]this invention -- to achieve the above objects -- (1) -- mainly -- general formula (I): [0008]

[Formula 2]



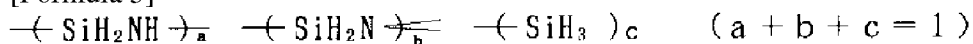
[0009](However, R¹, R², and R³ express independently the basis, the alkyl silyl group, alkylamino group, and alkoxy group a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, or whose basis directly linked with silicon out of these Motomochi is carbon, respectively.) It corrects, At least one of R¹, R², and R³ is a hydrogen atom. The constituent for coating, wherein the number average molecular weight which has a main skeleton which consists of a unit expressed is the solution which dissolved polysilazane and acrylic resin of 100-50,000 is provided. (2) -- in this constituent for coating (1), acrylic resin provides what is a thing containing the ingredient of methyl methacrylate.

[0010]Inorganic polysilazane whose polysilazane to be used needs to be polysilazane which has Si-H combination or N-H combination at least in intramolecular and whose all or ***** of R¹, R², and R³ is a hydrogen atom especially in general formula (I) (perhydropolysilazane) [For example, refer to JP,63-16325,B, JP,1-138108,A, 1-138107, 4-63833, and No. Japanese-Patent-Application-No. 3-320167.] Or although polysilazane (for example, the random copolymerization silazane of JP,3-31326,A, the poly siloxazane of JP,62-195024,A, the poly metalaw silazane of JP,2-77427,A, etc.) near it is preferred, the mixture of the copolymer of polysilazane and other polymer besides a polysilazane independent, or polysilazane and other compounds -- the feature of polysilazane, especially inorganic polysilazane -- ***** -- as long as -- it can use.

[0011]There is a chain, annular, a thing that has the structure of cross linkage, or a thing which has the structure of these plurality simultaneously in intramolecular in polysilazane to be used, and independent [these] or a mixture can also be used. Although there is the following as an example of representation of polysilazane to be used, it is not limited to these.

[0012]What has a hydrogen atom in R¹, R², and R³ by general formula (I), It is perhydropolysilazane and the manufacturing method is reported to Communication of Am.Cer.Soc., JP,63-16325,B, D.Seyferth et al., C-13, and January 1983. Although what is obtained by these methods is a mixture of polymer which has various structures, it contains a chain portion and an annular portion in intramolecular fundamentally, [0013]

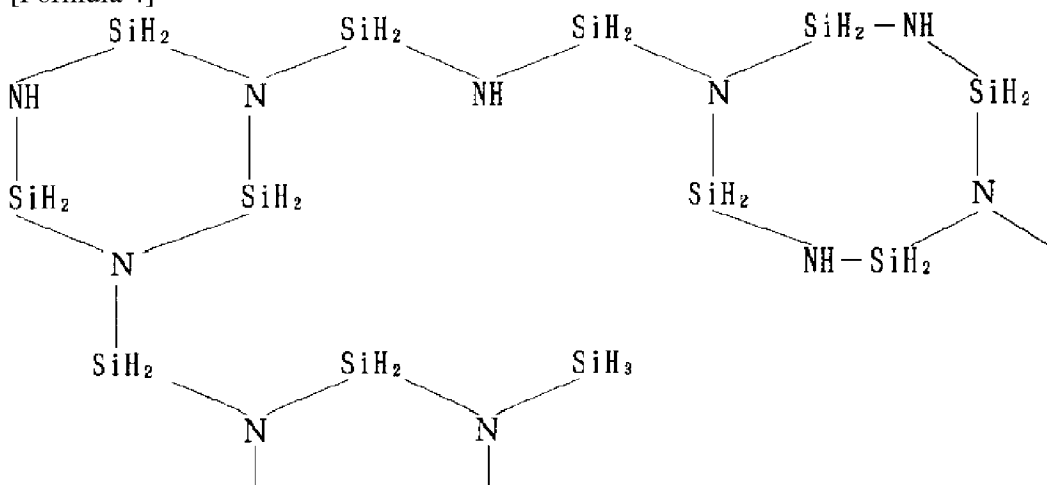
[Formula 3]



[0014]It can express with ***** . It is as following when an example of the structure of perhydropolysilazane is shown.

[0015]

[Formula 4]



[0016]The manufacturing method of the polysilazane which has a hydrogen atom in R^1 and R^2 , and has a methyl group in R^3 by general formula (I), D. It is reported to Polym.Prepr., Seyferth et al., Am.Chem.Soc., Div.Polym.Chem., and 25 and 10 (1984). As for the polysilazane obtained by this method, a repeating unit is linear polymer and cyclic polymer of $-(SiH_2NCH_3)-$, and neither has the structure of cross linkage.

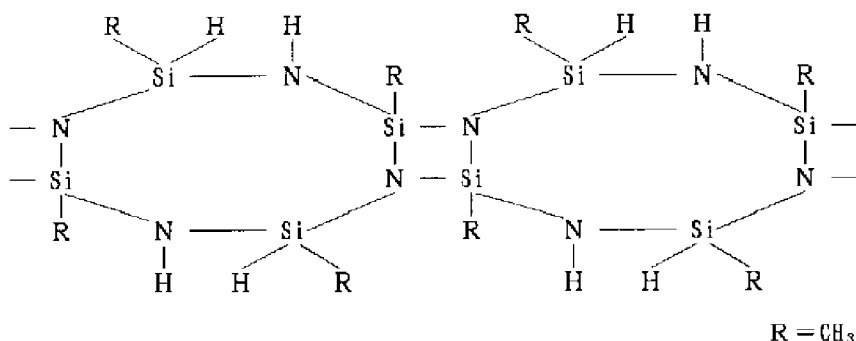
[0017]The manufacturing method of the polyorgano (hydronalium) silazane which has a hydrogen atom in R^1 and R^3 , and has an organic group in R^2 by general formula (I), D. It is reported to Polym.Prepr., Seyferth et al., Am.Chem.Soc., Div.Polym.Chem., 25 and 10 (1984), and JP,61-89230,A. That to which a degree of polymerization mainly has the cyclic structure of 3-5 by making $-(R^2SiH_2NH)-$ into a repeating unit in the polysilazane obtained by these methods, and $(R^3SiH_2NH)_x[(R^2SiH)_2N]_{1-x}$ The intramolecular which can be shown with the chemical formula of $1-x$ ($0.4 < x < 1$) has some which have chain structure and cyclic structure simultaneously.

[0018]Polysilazane which has an organic group in R^1 by general formula (I) at a hydrogen atom, R^2 , and R^3 , What has an organic group in R^1 and R^2 , and has a hydrogen atom in R^3 makes $-(R^1R^2SiNR^3)-$ a repeating unit, and a degree of polymerization mainly has the cyclic structure of 3-5. Although polysilazane to be used has a main skeleton which consists of a unit expressed with general formula (I) like the above, When a unit expressed with general formula (I) may circularize so that clearly [the above], the annular portion serves as an end group in that case and such circularization is not carried out, the end of a main skeleton can be the same basis as R^1 , R^2 , and R^3 , or hydrogen.

[0019]Some polyorgano (hydronalium) silazanes have the structure of cross linkage in intramolecular that Communication of Am.Cer.Soc., D.Seyferth et al., C-132, and July1984. are reported. It is as following when an example is shown.

[0020]

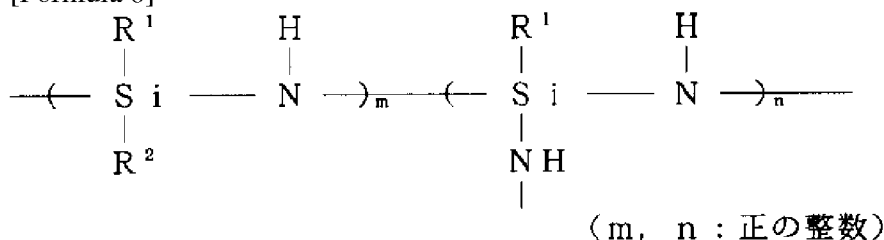
[Formula 5]



[0021] Polysilazane which has the structure of cross linkage obtained by ammonolysis of R^1SiX_3 (X: halogen) which is reported to JP,49-69717,A ($\text{R}^1\text{Si}(\text{NH})_x$), Or polysilazane which has the following structure acquired by ** ammonolysis of R^1SiX_3 and R^2_2SiX_2 can also be used as a charge of a start material.

[0022]

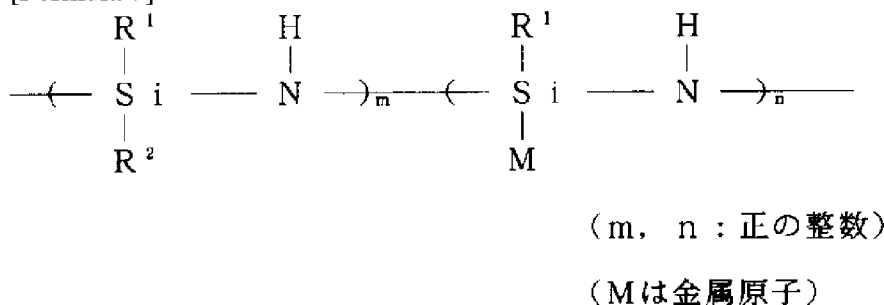
[Formula 6]



[0023] The poly metalaw silazane containing a metal atom can also be used as a charge of a start material like the following structure (M which is a metal atom of a side chain may be constructing the bridge among a formula).

[0024]

[Formula 7]



[0025] In addition, a repeating unit which is reported to JP,62-195024,A, $[(\text{SiH}_2)_n(\text{NH})_m]$ It reaches. $[(\text{SiH}_2)_r\text{O}]$ Poly siloxazane expressed with (the inside of a formula of these, n, m, and r are 1, 2, or 3, respectively), A poly rag silazane excellent in heat resistance which a boron compound is made to react to polysilazane which is reported to JP,2-84437,A, and is manufactured, A poly metalaw silazane which polysilazane and a metal alkoxide which are reported to JP,63-81122,A, 63-191832, and JP,2-77427,A are made to react, and is manufactured, JP,1-138108,A, 1-138107, 1-203429, Make a molecular weight which is reported to 1-203430, 4-63833, and 3-320167 increase, or (Front 4 persons of the above-mentioned gazette), An inorganic silazane high polymer and refining polysilazane which raised hydrolysis resistance (back 2 persons), JP,2-175726,A, 5-86200, 5-331293, A copolymerization silazane advantageous to thick-film-izing which introduced an organic component into polysilazane which is reported to 3-31326, JP,5-238827,A, JP,4-272020,A, 5-93275, 5-214268, 5-30750, Construction to metal which added or added a catalytic compound for promoting ceramics-ization to polysilazane which is reported to 5-

338524, such as plastics and aluminum, is possible, Cold cure type polysilazane etc. which are ceramics-ized more at low temperature can be used similarly.

[0026]When mixing polysilazane with an acrylic resin particle, polysilazane usually dissolves in a solvent. As a solvent, ether, such as halogenated hydrocarbon, such as a hydrocarbon solvent of aliphatic hydrocarbon, alicyclic hydrocarbon, and aromatic hydrocarbon, halogenation methane, halogenation ethane, and halogenated benzene, aliphatic series ether, and alicyclic ether, can be used. A desirable solvent A methylene chloride, chloroform, a carbon tetrachloride, bromoform, Halogenated hydrocarbon, such as ethylene chloride, an ethylidene chloride, trichloroethane, and tetrachloroethane, Ethyl ether, isopropyl ether, ethylbutyl ether, butyl ether, 1,2-dioxyethane, dioxane, dimethyldioxane, a tetrahydrofuran, Ether, such as tetrahydropyran, a cellosolve acetate, and carbitol acetate, It is hydrocarbon, such as pentanehexane, an isohexane, methylpentane, heptane, isoheptane, octane, isooctane, cyclopentane, methylcyclopentane, cyclohexane, a methylcyclohexane, benzene, toluene, xylene, and ethylbenzene, etc.

[0027]As acrylic resin to be used, although various kinds of resin can be used, For example, acrylic ester (as alcohol residue) A methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl group, An isobutyl group, t-butyl group, a 2-ethylhexyl group, a cyclohexyl group, ; methacrylic acid ester which can illustrate a phenyl group, benzyl, a phenylethyl group, etc. (alcohol residue is the same as the above); 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, A hydroxy content monomer like 2-hydroxypropyl methacrylate **; Acrylamide, Methacrylamide, N-methylmethacrylamide, N-methylacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N,N-dimethylolacrylamide, N-methoxymethyl acrylamide, Amide group containing monomer;N like N-methoxymethyl methacrylamide and N-phenylacrylamide **, N-diethylamino ethyl acrylate, An amino group content monomer like N,N-diethylamino ethyl methacrylate **; Glycidyl acrylate, glycidyl methacrylate. An epoxy group content monomer like allyl-glycidyl-ether **; Styrene sulfonic acid, vinylsulfonic acid and those salts (for example, sodium salt and potassium salt.) A monomer containing a sulfonic group like ** or its salts, such as ammonium salt; Crotonic acid, itaconic acid, acrylic acid, maleic acid, boletic acid, and those salts (for example, sodium salt.) A monomer containing a carboxyl group like ** or its salts, such as potassium salt and ammonium salt; A maleic anhydride, A monomer containing anhydrides, such as itaconic acid anhydride; In addition to this, a vinylisocyanate, An allylisocyanate, styrene, vinylmethyl ether, vinylethyl ether, Vinyltris alkoxysilane, alkyl maleic acid monoester, Although built with combination of monomers, such as alkyl boletic acid monoester, acrylonitrile, a methacrylonitrile, alkyl itaconic acid monoester, a vinylidene chloride, vinyl acetate, and VCM/PVC, an ingredient of an acrylic monomer like (meta-) an acrylic acid derivative and a methacrylic acid derivative -- more than 50 mol % -- what is contained is preferred and a thing containing especially an ingredient of methyl methacrylate is preferred. Acrylic resin, for example, polymethacrylic acid perfluoro t-butyl, containing fluoride, Polyperfluoro isopropyl methacrylate, polymethacrylic acid hexafluoro 2-propyl, polymethacrylic acid trifluoroethyl, a fluorination ester polymer of acrylic acid (meta), etc. have an advantage which is excellent in sliding nature and water repellence. A stable coating solution is obtained without this invention deteriorating polysilazane, if that polysilazane and acrylic resin dissolve and acrylic resin suitable moreover are chosen, Both transparency is efficiently employed as it is by it, and it finds out and succeeds in becoming possible about both demerit to obtain complementary ***** coating. As a solvent which can dissolve acrylic resin, ketone, such as flame-ized hydrogen, such as glycol ether, such as ester species, such as ethyl acetate and n-butyl acetate, cellosolve, and a cellosolve acetate, toluene, and xylene, acetone, and methyl ethyl ketone, can be mentioned.

[0028]What is necessary is just to generally mix a solution of polysilazane, and a solution of acrylic resin, when creating a solution for coating containing polysilazane and acrylic resin. Loadings of polysilazane and acrylic resin are total solids, when it can choose widely according to a use of coating, for example, thinks flexibility as important. When making [the total quantity of polysilazane and acrylic resin] into 100 % of the weight, and carrying out polysilazane 3 to 30% of the weight of within the limits and thinking hardness and heat resistance as important, 30 to 97% of the weight of within the limits is good. [Quantity of acrylic resin is the quantity except quantity of polysilazane among the above-mentioned amounts of solid content.]

As a solvent which dissolves polysilazane and acrylic resin, what dissolves both polysilazane and acrylic resin stably is preferred, for example, xylene, toluene, butylcarbitol acetate, n-butyl acetate, etc. are preferred. When using a solvent, in order to adjust solubility of said acrylic resin addition polysilazane, and a vapor rate of a solvent, two or more kinds of solvents may be mixed. The amount of solvent used (comparatively) is chosen by thickness to need, and changes with an average molecular weight of polysilazane, molecular weight distribution, and its structures so that workability may become good with a coating method to adopt, but. Generally, a solvent in a constituent for coating is mixable about 99 to 5% of the weight in the range whose solids concentration is 1 to 95 % of the weight. It is solids concentration 5-60 pile degree % preferably. In this invention, although it is not indispensable, a suitable bulking agent may be added if needed. As an example of a bulking agent, fines of non-oxide stock inorganic substances, such as oxide stock inorganic substances including silica, alumina, zirconia, and mica or silicon carbide, and silicon nitride, etc. are mentioned. Depending on a use, addition of metal powder, such as aluminum, zinc, and copper, is also possible. If an example of a bulking agent is furthermore described in detail, silica, quartz, a novaculite, silica system: of diatomaceous earth etc. -- synthetic-amorphous-silica: -- kaolinite and mica. Silicates, such as talc, wollastonite, asbestos, a calcium silicate, and aluminum silicate : Glass powder, Vitreous humours, such as a glass bulb, a hollow glass ball, a glass flake, and a foam glass ball : Boron nitride, Boron carbide, alumimium nitride, aluminium carbide, silicon nitride, silicon carbide, Non-oxide stock inorganic substance:calcium carbonate, such as titanium boride, titanium nitride, and titanium carbide : A zinc oxide, Metallic oxides, such as alumina, magnesia, titanium oxide, and beryllium oxide : Barium sulfate, Metal powder, such as molybdenum disulfide, a tungsten disulfide, other inorganic-substance [fluoridation carbon and]:aluminum, bronze, lead, a stainless steel, and zinc: Carbon objects, such as carbon black, corks, black lead, pyrolytic carbon, and a hollow carbon ball, etc. are raised.

[0029]a thing of various shape, such as that these bulking agents are needlelike (a whisker is included.), a grain, and the shape of a scale, -- it can be independent, or two or more sorts can be mixed, and it can use. As for a size of particles of these bulking agents, it is desirable that it is smaller than thickness which can be applied at once. An addition of a bulking agent is the range of 0.05 weight section - ten weight sections to a total of one weight section of acrylic resin and polysilazane, and especially a desirable addition is the range of 0.2 weight sections - three weight sections. It may be used by coupling agent processing, vacuum evaporation, plating, etc., carrying out the surface treatment of the surface of a bulking agent.

[0030]A various paints and leveling agent, a defoaming agent, a spray for preventing static electricity, an ultraviolet ray absorbent, a pH adjuster, a dispersing agent, a surface modifier, a plasticizer, a dryer, and an antisagging agent may be added to a constituent for coating if needed. In this way, on a base, 1 time or after applying repeatedly twice or more, a constituent for coating of created this invention is printed, and forms coating membrane.

[0031]A base in particular that applies a coating composition may not be limited, but any, such as metal, ceramics, and plastics, may be sufficient as it. As an application

means as coating, the usual coating method, i.e., immersion, a spin coat, roll coating, bar coating, brush coating, spray coating, flow coating, etc. are used. If the surface treatment of the base is carried out by a file cliff, degreasing, various blasts, etc. before spreading, adhesion performance of a coating composition will improve.

[0032]It heats and calcinates, after coating with such a method and making it dry enough. Although it oxidizes and hydrolyzes, polysilazane is hardened depending on bridge construction, condensation, or a firing environments by this calcination and a ceramics phase is formed, Acrylic resin can carry out heat softening simultaneously, and a precise film composite(comparing with composite which adds an inorganic filler etc.)-ized on a structure level with a detailed organic portion which consists of a ceramics phase which makes a subject Si-O combination or Si-N combination, and an acrylic phase can be obtained.

[0033]As for calcination temperature, it is preferred that it is the temperature which ceramics-ization of polysilazane evolves and is fully hardened. Although this is about 400 ** preferably, since softening temperature of an acrylic resin or decomposition temperature is low, it is usually common to calcinate [not less than 300 **] at 100-300 **. Therefore, what is necessary is for low-temperature ceramics-ized type polysilazane, such as Japanese Patent Application No. No. 93275 [five to], to be needed in order to make polysilazane ceramics-ize thoroughly, but just to choose polysilazane according to a use. The above-mentioned firing condition changes with molecular weights and structures of polysilazane. A heating rate in particular is not limited. Although firing environments may be any, such as inside of oxygen and the air, or inactive gas, inside of the air is more preferred. Hydrolysis by a steam which lives together in oxidation of polysilazane or the air by calcination in the air advances.

[0034]If polysilazane and acrylic resin are combined like the above according to this invention, the inorganic matter / organic coating hybridized on a detailed structure level will be obtained. Especially inorganic polysilazane (perhydropolysilazane) especially is excellent in heat resistance, hardness, and adhesion, combination with acrylic resin which makes elongation the feature is the multicomputer system which maintained balance with which mutual demerit is compensated, and the characteristic which exceeds the existing multicomputer system coating is given.

[0035]When using combination of perhydropolysilazane and acrylic resin, this, Since the state where perhydropolysilazane and acrylic resin which dissolved in xylene dissolved uniformly unlike what is called compound resin that adds a glass filler etc. is made into a starting point, It is expected that amorphous $\text{SiO}_2/\text{Si}_3\text{N}_4$, and acrylic

resin have composite-ized on a level of a very homogeneous and detailed structure, Since acrylic resin becomes soft at the time of contraction accompanying ceramics-izing of perhydropolysilazane and it follows, it is thought that it is because a precise film without a pinhole is easy to be obtained.

[0036]According to this invention, it is easy to control balance of minerals (ceramics) and an organic matter (acrylic resin). Since it composite-izes on a structure level uniform [ceramics and acrylic resin based on polysilazane] like the above, and detailed, a rate of minerals and quality of organicity can choose in the wide rate range -- heat resistance and hardness -- importance -- ***** -- the characteristic which was wide range and was excellent from a thing to a thing with emphasis on flexibility is realizable.

[0037]Since polysilazane serves as amorphous ceramics with the low calcination post heating rate of expansion, Although a thickness limit is low in a problem of matching with a metal substrate etc. to a simple substance, since acrylic resin has the high coefficient of thermal expansion, matching with a various base is possible, therefore a 10-100-micrometer thick film can construct easily in a constituent for coating of this invention. It is as following when amorphous ceramics after calcination of polysilazane and the characteristic of acrylic resin are summarized by comparison.

[0038]

Polysilazane (after-calcination amorphous ceramics) Acrylic resin.

----- Hardness It is high. It is low. Flexibility (elongation) It is very low. It is high. Heat resistance It is very high. It is low. Coefficient of thermal expansion It is very low. It is high. Adhesion It is very high. It is comparatively bad. Ceramic yield It is very high. - Contraction It is comparatively low. - Heat characteristic Heat-curing heat softening, melting, heat curing[0039]

[Example]

Example 1 Mitsubishi Rayon make acrylic resin BR-71 was dissolved in xylene, and it was considered as the 10wt% solution. Next, it mixed with the stirrer so that it might become PHPS:BR 71= 6:4 (wt), and the 20wt% xylene solution of TONEN perhydropolysilazane PHPS-1 and the 10wt% xylene solution of BR-71 were used as water-white coating fluid. It constructed with flow coating using this coating fluid to SUS304 and Cu board which 150x50x0.4-mm^t degreased, and dried for 10 minutes at the room temperature. Next, printing was carried out at 300 ** for 1 hour (it is temperature up at a part for 10 **/), and ceramics / acrylic resin system coat with a water-white thickness of about 2 micrometers were obtained. The hardness of this coat was >9H (SUS304 substrate). When the spectral luminous intensity of the coat (1 micrometer in thickness) which carried out the spin coat to the silica glass of 30x30x1.1-mm^t (2000rpm x20sec), and was able to be printed at 300 ** for 1 hour was measured, the visible light transmittance at 500 nm was 96%. Next, when the bending test was carried out, SUS304 substrate and Cu board were 5T success. Only the conditions of the example 2 following were changed and ceramics / acrylic resin system water-white film was constructed by the same technique as Example 1. The PHPS:BR 71= 5:5 (wt) evaluation result was as follows.

hardness; -- 9H visible-light-transmittance (@500nm); -- 95% bending nature; after adjusting coating fluid so that it may become PHPS:BR 71= 6:4 (wt) about the 40wt% xylene solution of 1T success example 3PHPS-1, and the 15wt% xylene solution of BR-71, It constructed with flow coating to SUS304 substrate. When calcinated at 300 ** for 1 hour, 10 micrometers of thickness, and the ceramics / acrylic resin system water-white film of hardness >9H were obtained.

0.5wt% (as opposed to the polysilazane 100) of acetic acid Pd was made to add to Examples 4-9 and comparative example PHPS-1. The 20wt% xylene solution of low-temperature ceramic type polysilazane and the 10wt% xylene solution of BR80 were mixed at a following rate.

PHPS : BR 80

実施例 4	8	2
実施例 5	6	4
実施例 6	4	6
実施例 7	2	8
実施例 8	1	9
実施例 9	0. 5	9. 5
比較例	0	10

When the above-mentioned coating fluid was constructed to SUS304 substrate like Example 1 and 200 ** x 1h were able to be printed, as for any sample, the water-white film of 2-3 micrometers of thickness was obtained. The following result was obtained when the hardness of these coats was measured.

** degree ----- example 4 >9H example 5 >9H example 6 >9H example 7 >9H example 8 9H example 9 9H comparative example 4H [0040]

[Effect of the Invention]In this invention, polysilazane resin and an acrylic resin were changed into the compatible state.

Therefore, the transparent coat in which both feature was employed efficiently was

obtained, without reducing the characteristic of polysilazane.

As a result, inorganic matter / organic hybrid film excellent in heat resistance, hardness, adhesion, flexibility, the thickness limit, and the price can be obtained easily.

[Translation done.]